

PATENT ABSTRACTS OF JAPAN

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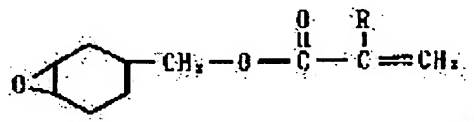
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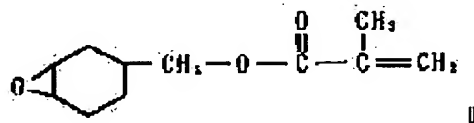
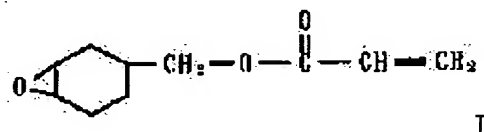
(54) PHOTOCURABLE OLIGOMER, RESIN COMPOSITION CONTAINING SAME, AND ITS CURED ARTICLE

(57)Abstract:

PURPOSE: To obtain a photocurable oligomer which gives a printing ink excellent in gloss, pigment dispersion, printability, etc., by reacting a specific compd. with rosin.



CONSTITUTION: A photocurable oligomer is prepd. by reacting a compd. of formula I (wherein R is H or CH3) (e.g. a compd. of formula II or III) with rosin. The type of rosin used is determined considering the rate of ultraviolet curing of the resulting ink, the hue of the oligomer, etc., and usually rosins with conjugated double bonds stabilized, such as a hydrogenated rosin or a disproportionated rosin, are suitable. The oligomer can be used for various applications by utilizing its photocurability and gives, when used as a binder, a printing ink excellent in gloss, pigment dispersion, printability, etc., in comparison with conventional solvent-based printing inks.



LEGAL STATUS

[Date of request for examination]

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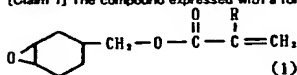
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CLAIMS

[Claim(s)]

[Claim 1] The compound expressed with a formula (1) [** 1]



(— R is H or CH₃ among a formula.) --- photoresist oligomer which is a reactant with rosin.

[Claim 2] The resin constituent characterized by containing photoresist oligomer according to claim 1.

[Claim 3] The hardened material of a resin constituent according to claim 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to new photoresist oligomer, the resin constituent using this, and its hardened material. In more detail, it is the oligomer which has ultraviolet-rays hardenability, and is related with the resin constituent and hardened material using the photoresist oligomer and this suitable for especially the binder for printing ink.

[0002]

[Description of the Prior Art] The ultraviolet curing ink is known as a constituent which blends suitably reactant diluents, such as trimethylolpropane triacrylate, a photopolymerization initiator, a pigment, etc. with the partial saturation epoxy resin ester usually reacted and obtained in an epoxy resin and an acrylic acid, and is obtained. In this, although partial saturation epoxy resin ester, unsaturated polyester, etc. are positioned as oligomer in the binder for ink, since this oligomer relates to many ink properties acquired [cure rate / gloss, pigment dispersibility, viscosity, a printability,] closely, it is important also especially in said constituent.

[0003]

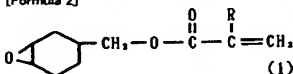
[Problem(s) to be Solved by the Invention] In recent years, even if it is an ultraviolet curing ink, it is required that it should have a printability comparable as conventional solvent mold ink, and it is in the situation that it cannot be satisfied with the partial saturation epoxy resin which is conventional polyfunctional oligomer of this demand enough.

[0004] For example, as a partial saturation epoxy resin, although the reactant of the epoxy resin of bisphenol A and an acrylic acid (meta) is known, when an ultraviolet curing ink is prepared using this, there is a fault that emulsification and the misting phenomenon of ink are especially accepted notably among printabilities. Therefore, development of the new oligomer which can offer the ultraviolet-rays hardenability ink which has the outstanding printability is demanded.

[0005]

[Means for Solving the Problem] With the conventional technique, this invention is made in order to be able to solve and to solve the inside **** aforementioned technical problem. This invention persons found out that said technical problem could be solved by using the specific oligomer which has a resin component in a side chain, as a result of repeating research wholeheartedly that the outstanding photoresist oligomer with which can be satisfied of these many engine performance should be developed in consideration of a cure rate besides a printability, stability on board, etc. That is, this invention is a compound [0006] expressed with 1. type (1).

[Formula 2]



[0007] (— they are the inside R and H of a formula, or CH₃) — it is related with the hardened material of the resin constituent characterized by containing the photoresist oligomer and the photoresist oligomer given in 2. 1st term which are a reactant with resin, and a resin constituent

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acetophenone, 2-hydroxy - Photopolymerization initiators, such as 2-methyl-1-phenyl propane-1-ON, usually among a resin constituent 0.5 - 20 % of the weight. It is desirable to use aliphatic series, aromatic amine or 4, and 4-screw diethylamino benzophenone etc. as an accelerator 0.1 to 10% of the weight among a resin constituent if needed furthermore.

[0015] Furthermore, a part of epoxy (meta) acrylate known from the former other than the photoresist oligomer of this invention, urethane (meta) acrylate, etc. can also be used together as a resin constituent of this invention. By adding said reaction diluent etc. further and hypoviscosity-izing it further, etc., the resin constituent of this invention can be used as a coating, adhesives, a solder resist, an overprint varnish, etc., and can also be further used as a charge of moldings lumber. The resin constituent of this invention can be obtained by mixing each component to homogeneity. The hardened material of the resin constituent of this invention can be obtained by irradiating ultraviolet rays or an electron ray with a conventional method, and making it harden.

[0016]

[Example] An example explains this invention to a detail further below. The section shows the weight section among an example.

The example 1 colorlessness rosin (product [made from Arakawa Chemical industry], KR-610, disproportionation rosin, acid number 170 (mgKOH/g)) 200 section, the compound 115 section of said formula (2), the methyl triethyl ammoniumchloride 1.14 section, and the METOKINON 0.3 section are taught, temperature up is carried out to 95 degrees C, and it reacts at 95 degrees C. It reacted until the acid number (mgKOH/g) of reaction mixed liquor became five or less (about 25 hours), and the photoresist oligomer (product A) of this invention was obtained. The result of having measured according to the high-resolution nuclear magnetic resonance (NMR) of the obtained product is shown below.

[0017]

No. PPM No. PPM 1 166.220 9 124.251 2 166.160 10 124.032 3 146.713 11 77.484 4 145.733 12 77.061 5 [130.712] 13 76.636 6 128.419 14 72.913 7 128.310 15 72.832 8 127.001 16 71.989 No. PPM No. PPM 17 71.707 45 36.872 18 71.662 46 36.741 19 68.352 47 36.695 20 68.181 48 36.555 21 68.049 36.346 22 67.493 50 36.243 23 67.274 51 35.390 24 67.225 52 34.434 25 67.138 53 33.454 26 67.075 33.338 27 67.028 55 33.092 28 56.260 56 32.808 29 49.989 57 32.611 30 47.785 58 32.125 31 47.713 59 32.012 46.521 60 31.839 33 45.114 61 31.790 34 44.224 62 31.738 35 43.661 63 30.800 36 40.462 64 30.724 37 40.379 65 30.355 38 38.423 66 29.832 39 38.228 67 28.785 40 38.137 68 28.709 41 37.906 69 28.635 42 37.167 70 27.834 43 37.053

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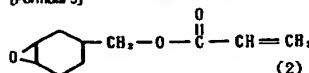
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given in 3. 2nd term.

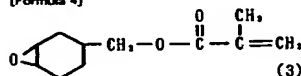
[0008] The new photoresist oligomer of this invention can be obtained by making the compound and rosin which are expressed with said formula (1) react. As an example of a compound expressed with a formula (1), it is [0009].

[Formula 3]



[0010]

[Formula 4]



[0011] ***** — things are made. The rosin which was determined in consideration of the ultraviolet-rays cure rate of the ink obtained, the color tone of photoresist oligomer, etc., and usually carried out stabilizing treatment of the conjugated double bond, such as hydrogenation rosin and disproportionation rosin, is suitable for rosin. For example, the product made from Arakawa Chemical industry, a trade name, HAPE-RU (hydrogenation rosin), KR-610 (colorless rosin), etc. can be mentioned.

[0012] The reaction of the compound and rosin which are expressed with a formula (1) performs preferably about 0.9-1.5Eq of compounds expressed with a formula (1) to 1Eq of the carboxyl group of rosin by the ratio which becomes about 0.95-1.1Eq preferably especially. In order to promote a reaction, it is desirable to use catalysts (for example, triethylamine, benzyl dimethylamine, methyl triethyl ammoniumchloride, triphenylphosphine, etc.), and the amount of this catalyst used is 0.3 - 5 % of the weight especially preferably 0.1 to 10% of the weight preferably to reaction raw material mixture. In order to prevent the polymerization under reaction, it is desirable to use polymerization inhibitors (for example, METOKINON, hydroquinone, phenothiazin, etc.), and the amount used is 0.05 - 0.5 % of the weight especially preferably 0.01 to 1% of the weight preferably to reaction raw material mixture. 60-150 degrees C of reaction temperature are 80-120 degrees C especially preferably. Moreover, reaction time is 10 - 50 hours especially preferably for 5 to 60 hours.

[0013] Since hyperviscosity [the resin constituent of this invention / photoresist oligomer] it usually uses a reactant diluent in the range of the 20 - 700 weight section to the photoresist oligomer 100 weight section of this invention if needed for the purpose of a viscosity drop. As this reactant diluent, 2-hydroxyethyl (meta) acrylate, Tripropylene glycol di(meth)acrylate, hydroxy pivalate neopentyl glycol di(meth)acrylate, Bisphenol A tetra-ETOKISHUJI (meta) acrylate, bisphenol F tetra-ETOKISHUJI (meta) acrylate, Trimethylol propane TORI (meta) acrylate, trimethylol propane TORIPUROPOKISHITORI (meta) acrylate, Ditrimehtylol propane tetrapod (meta) acrylate, tricyclodecanedimethylol di(meth)acrylate, dipentaerythritol hexa, PENTA (meta) acrylate, etc. can be mentioned. these reactivity diluent — one sort — or two or more sorts can be used.

[0014] When using the resin constituent of this invention as printing and a binder for ink, pigments, such as fast eroticism -, benzidine eroticism -, Lake Red 4R, Lake Red C, brilliant carmine 6B, a copper phthalocyanine blue, a titanium white, and carbon black, can usually be further distributed and used at 50 or less % of the weight among the resin constituent of this invention if needed. Furthermore, extenders, such as an alumina and silicon, may be distributed and used, moreover, in case [like ultraviolet rays] the activity energy line of low energy is comparatively used as a hardening energy line A benzophenone, a thioxan ton, benzoin ethyl ether, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropane-1-ON, A diethoxy

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No.	PPM
73	25. 396
74	24. 812
75	24. 625
76	24. 426
77	23. 966
78	23. 902
79	22. 748
80	21. 823
81	21. 708
82	21. 622
83	21. 369
84	21. 302
85	19. 826
86	19. 774
87	19. 594
88	19. 312
89	19. 046
90	18. 627
91	18. 192
92	18. 090
93	16. 828
94	16. 587
95	14. 635
96	14. 522
97	0

71 27.131 44 37.014 72 26.087

[0018] In addition, the solvent performed the above-mentioned measurement by the proton decoupling method using heavy chloroform, using a tetramethylsilane as a reference material. [0019] The example 2 colorlessness rosin (product [made from Arakawa Chemical industry], KR-610, disproportionation rosin, acid number 170 (mgKOH/g)) 200 section, the compound 124 section of said formula (3), the triphenyl phosphine 1.16 section, and the METOKINON 0.32 section were taught, it reacted at 95 degrees C (about 25 hours), and the photoresist oligomer (product B) of this invention was obtained. In ordinary temperature, Product B was a solid-state and was light yellow transparency.

N. Measurement result of M.R. [0020]

No. PPM No. PPM 1 178.358 20 77.054 2 178.000 21 76.631 3 167.483 22 72.950 4 167.418 23 72.874 5 167.369 24 72.498 6 146.706 25 71.996 26 71.901 27 71.733 28 71.682 29 71.633 30 71.584 31 71.535 32 71.486 33 71.437 34 71.388 35 71.339 36 71.290 37 71.241 38 71.192 39 71.143 40 71.094 41 71.045 42 70.996 43 70.947 44 70.898 45 70.849 46 70.800 47 70.751 48 70.702 49 70.653 50 70.604 51 70.555 52 70.506 53 70.457 54 70.408 55 70.359 56 70.310 57 70.261 58 70.212 59 70.163 60 70.114 61 70.065 62 70.016 63 69.967 64 69.918 65 69.869 66 69.820 67 69.771 68 69.722 69 69.673 70 69.624 71 69.575 72 69.526 73 69.477 74 69.428 75 69.379 76 69.330 77 69.281 78 69.232 79 69.183 80 69.134 81 69.085 82 69.036 83 68.987 84 68.938 85 68.889 86 68.840 87 68.791 88 68.742 89 68.693 90 68.644 91 68.595 92 68.546 93 68.497 94 68.448 95 68.399 96 68.350 97 68.301

8628.728 60 37.014 87 28.470 61 36.940 88 27.996 36.732 89 27.883 63 36.653 90 27.188 64

8628.728 60 37.014 87 28.470 61 36.940 88 27.996 36.732 89 27.883 63 36.653 90 27.188 64

8628.728 60 37.014 87 28.470 61 36.940 88 27.996 36.732 89 27.883 63 36.653 90 27.188 64

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8628.728 60 37.014 87 28.470 61 36.940 88 27.996 36.732 89 27.883 63 36.653 90 27.188 64

36.558 91 26.092 65 36.349 92 25.401

Misting : 1200 revolutions of rolls to which paper was put and ink adhered before the roll of an

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[Effect of the Invention] The photoresist oligomer of this invention has the advantage which was excellent in points, such as gloss of the obtained printing ink, pigment dispersibility, and a printability, as compared with conventional solvent mold printing ink, when it is applicable to a wide range application and is especially used as a binder for printing ink by using the photoresist.

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